WAC 296-62-07525 Appendix A substance safety data sheet--Benzene.

(1) **Substance identification.**

(a) Substance: Benzene.

(b) Permissible exposure: Except as to the use of gasoline, motor fuels, and other fuels subsequent to discharge from bulk terminals and other exemptions specified in WAC 296-62-07523 (1)(b):

(i) Airborne: The maximum time-weighted average (TWA) exposure limit is one part of benzene vapor per million parts of air (1 ppm) for an eight-hour workday and the maximum short-term exposure limit (STEL) is 5 ppm for any fifteen-minute period.

(ii) Dermal: Eye contact shall be prevented and skin contact with liquid benzene shall be limited.

(c) Appearance and odor: Benzene is a clear, colorless liquid with a pleasant, sweet odor. The odor of benzene does not provide adequate warning of its hazard.

(2) **Health hazard data.**

(a) Ways in which benzene affects your health. Benzene can affect your health if you inhale it, or if it comes in contact with your skin or eyes. Benzene is also harmful if you happen to swallow it.

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(b) Effects of overexposure.

(i) Short-term (acute) overexposure: If you are overexposed to high concentrations of benzene, well above the levels where its odor is first recognizable, you may feel breathless, irritable, euphoric, or giddy; you may experience irritation in eyes, nose, and respiratory tract. You may develop a headache, feel dizzy, nauseated, or intoxicated. Severe exposures may lead to convulsions and loss of consciousness.

(ii) Long-term (chronic) exposure. Repeated or prolonged exposure to benzene, even at relatively low concentrations, may result in various blood disorders, ranging from anemia to leukemia, an irreversible, fatal disease. Many blood disorders associated with benzene exposure may occur without symptoms.

(3) **Protective clothing and equipment.**

(a) Respirators. Respirators are required for those operations in which engineering controls or work practice controls are not feasible to reduce exposure to the permissible level. However, where employers can document that benzene is present in the workplace less than thirty days a year, respirators may be used in lieu of engineering controls. If respirators are worn, they must have joint Mine Safety and Health Administration and the National Institute for Occupational Safety and Health (NIOSH) seal of approval, and cartridge or canisters must be replaced before the end of their service life, or the end of the shift, whichever occurs first. If you experience difficulty breathing while wearing a respirator, you may request a positive pressure respirator from your employer. You must be thoroughly trained to use the assigned respirator, and the training will be provided by your employer.

(b) Protective clothing. You must wear appropriate protective clothing (such as boots, gloves, sleeves, aprons, etc.,) over any parts of your body that could be exposed to liquid benzene.

(c) Eye and face protection. You must wear splash-proof safety goggles if it is possible that benzene may get into your eyes. In addition, you must wear a face shield if your face could be splashed with benzene liquid.

(4) **Emergency and first aid procedures.**

(a) Eye and face exposure. If benzene is splashed in your eyes, wash it out immediately with large amounts of water. If irritation persists or vision appears to be affected see a doctor as soon as possible.

(b) Skin exposure. If benzene is spilled on your clothing or skin, remove the contaminated clothing and wash the exposed skin with large amounts of water and soap immediately. Wash contaminated clothing before you wear it again.

(c) Breathing. If you or any other person breathes in large amounts of benzene, get the exposed person to fresh air at once. Apply artificial respiration if breathing has stopped. Call for medical assistance or a doctor as soon as possible. Never enter any vessel or confined space where the benzene concentration might be high without proper safety equipment and at least one other person present who will stay outside. A life line should be used.

(d) Swallowing. If benzene has been swallowed and the patient is conscious, do not induce vomiting. Call for medical assistance or a doctor immediately.

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(5) **Medical requirements.** If you are exposed to benzene at a concentration at or above 0.5 ppm as an 8-hour time-weighted average, or have been exposed at or above 10 ppm in the past while employed by your current employer, your employer is required to provide a medical examination and history and laboratory tests within sixty days of the effective date of this standard and annually thereafter. These tests shall be provided without cost to you. In addition, if you are accidentally exposed to benzene (either by ingestion, inhalation, or skin/eye contact) under emergency conditions known or suspected to constitute toxic exposure to benzene, your employer is required to make special laboratory tests available to you.

(6) **Observation of monitoring.** Your employer is required to perform measurements that are representative of your exposure to benzene and you or your designated representative are entitled to observe the monitoring procedure. You are entitled to observe the steps taken in the measurement procedure, and to record the results obtained. When the monitoring procedure is taking place in an area where respirators or personal protective clothing and equipment are required to be worn, you or your representative must also be provided with, and must wear the protective clothing and equipment.

(7) **Access to records.** You or your representative are entitled to see the records of measurements of your exposure to benzene upon written request to your employer. Your medical examination records can be furnished to yourself, your physician, or designated representative upon request by you to your employer.

(8) **Precautions for safe use, handling, and storage.** Benzene liquid is highly flammable. It should be stored in tightly closed containers in a cool, well ventilated area. Benzene vapor may form explosive mixtures in air. All sources of ignition must be controlled. Use nonsparking tools when opening or closing benzene containers. Fire extinguishers, where provided, must be readily available. Know where they are located and how to operate them. Smoking is prohibited in areas where benzene is used or stored. Ask your supervisor where benzene is used in your area and for additional plant safety rules.

[Statutory Authority: Chapter 49.17 RCW. 88-21-002 (Order 88-23), 296-62-07525, filed 10/6/88, effective 11/7/88.]

WAC 296-62-07527 Appendix B substance technical guidelines--Benzene.

(1) **Physical and chemical data.**

(a) Substance identification.

(i) Synonyms: Benzol, benzole, coal naphtha, cyclohexatriene, phene, phenyl hydride, pyrobenzol. (Benzin, petroleum benzin and Benzine do not contain benzene.)

(ii) Formula: C_6H_6 (CAS Registry Number: 71-43-2).

(b) Physical data.

(i) Boiling point (760 mm Hg); 80.1 C (176 F).

(ii) Specific gravity (water = 1): 0.879.

(iii) Vapor density (air = 1): 2.7.

(iv) Melting point: 5.5 C (42 F).

(v) Vapor pressure at 20 C (68 F): 75 mm Hg.

(vi) Solubility in water: .06%.

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(vii) Evaporation rate (ether = 1): 2.8.

(viii) Appearance and odor: Clear, colorless liquid with a distinctive sweet odor.

(2) **Fire, explosion, and reactivity hazard data.**

(a) Fire.

(i) Flash point (closed cup): -11 C (12 F).

(ii) Autoignition temperature: 580 C (1076 F).

(iii) Flammable limits in Air. % by volume: Lower: 1.3%, Upper: 7.5%.

(iv) Extinguishing media: Carbon dioxide, dry chemical, or foam.

(v) Special fire-fighting procedures: Do not use solid stream of water, since stream will scatter and spread fire. Fine water spray can be used to keep fire-exposed containers cool.

(vi) Unusual fire and explosion hazards: Benzene is a flammable liquid. Its vapors can form explosive mixtures. All ignition sources must be controlled when benzene is used, handled, or stored. Where liquid or vapor may be released, such areas shall be considered as hazardous locations. Benzene vapors are heavier than air; thus the vapors may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which benzene is handled.

(vii) Benzene is classified as a 1 B flammable liquid for the purpose of conforming to the requirements of WAC 296-24-330. A concentration exceeding 3,250 ppm is considered a potential fire explosion hazard. Locations where benzene may be present in quantities sufficient to produce explosive or ignitable mixtures are considered Class I Group D for the purposes of conforming to the requirements of WAC 296-24-95613.

(b) Reactivity.

(i) Conditions contributing to instability: Heat.

(ii) Incompatibility: Heat and oxidizing materials.

(iii) Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide).

(3) **Spill and leak procedures.**

(a) Steps to be taken if the material is released or spilled. As much benzene as possible should be absorbed with suitable materials, such as dry sand or earth; benzene remaining must be flushed with large amounts of water. Do not flush benzene into a confined space, such as a sewer, because of explosion danger. Remove all ignition sources. Ventilate enclosed places.

(b) Waste disposal method. Disposal methods must conform to other jurisdictional regulations. If allowed, benzene may be disposed of:

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(i) By absorbing it in dry sand or earth and disposing in a sanitary landfill;

(ii) If small quantities, by removing it to a safe location from buildings or other combustible sources, pouring it in dry sand or earth and cautiously igniting it; and

(iii) If large quantities, by atomizing it in a suitable combustion chamber.

(4) **Miscellaneous precautions.**

(a) High exposure to benzene can occur when transferring the liquid from one container to another. Such operations should be well ventilated and good work practices must be established to avoid spills.

(b) Use nonsparking tools to open benzene containers which are effectively grounded and bonded prior to opening and pouring.

(c) Employers must advise employees of all plant areas and operations where exposure to benzene could occur. Common operations in which high exposures to benzene may be encountered are: The primary production and utilization of benzene, and transfer of benzene.

[Statutory Authority: RCW 49.17.010, .040, .050. 02-12-098 (Order 00-20), § 296-62-07527, filed 06/05/02, effective 08/01/02. Statutory Authority: Chapter 49.17 RCW. 88-21-002 (Order 88-23), 296-62-07527, filed 10/6/88, effective 11/7/88.]

WAC 296-62-07529 Appendix C medical surveillance guidelines for benzene.

(1**)** **Route of entry. Inhalation; skin absorption.**

(2) **Toxicology.** Benzene is primarily an inhalation hazard. Systemic absorption may cause depression of the hematopoietic system, pancytopenia, aplastic anemia, and leukemia. Inhalation of high concentrations can affect central nervous system function. Aspiration of small amounts of liquid benzene immediately causes pulmonary edema and hemorrhage of pulmonary tissue. There is some absorption through the skin. Absorption may be more rapid in the case of abraded skin, and benzene may be more readily absorbed if it is present in a mixture or as a contaminant in solvents which are readily absorbed. The defatting action of benzene may produce primary irritation due to repeated or prolonged contact with the skin. High concentrations are irritating to the eyes and the mucous membranes of the nose, and respiratory tract.

(3) **Signs and symptoms.** Direct skin contact with benzene may cause erythema. Repeated or prolonged contact may result in drying, scaling dermatitis, or development of secondary skin infections. In addition, there is benzene absorption through the skin. Local effects of benzene vapor or liquid on the eye are slight. Only at very high concentrations is there any smarting sensation in the eye. Inhalation of high concentrations of benzene may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation, and/or giddiness, followed by a period of depression, drowsiness, or fatigue. A sensation of tightness in the chest accompanied by breathlessness may occur and ultimately the victim may lose consciousness. Tremors, convulsions, and death may follow from respiratory paralysis or circulatory collapse in a few minutes to several hours following severe exposures.

The detrimental effect on the blood-forming system of prolonged exposure to small quantities of benzene vapor is of extreme importance. The hematopoietic system is the chief target for benzene's toxic effects which are manifested by alterations in the levels of formed elements in the peripheral blood. These effects have occurred at concentrations of benzene which may not cause irritation of mucous membranes, or any unpleasant sensory effects. Early signs and symptoms of benzene morbidity are varied, often not readily noticed and nonspecific. Subjective complaints of headache, dizziness, and loss of appetite may precede or

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follow clinical signs. Rapid pulse and low blood pressure, in addition to a physical appearance of anemia, may accompany a subjective complaint of shortness of breath and excessive tiredness. Bleeding from the nose, gums, or mucous membranes, and the development of purpuric spots (small bruises) may occur as the condition progresses. Clinical evidence of leukopenia, anemia, and thrombocytopenia, singly or in combination, has been frequently reported among the first signs.

Bone marrow may appear normal, aplastic, or hyperplastic, and may not, in all situations, correlate with peripheral blood forming tissues. Because of variations in the susceptibility to benzene morbidity, there is no "typical" blood picture. The onset of effects of prolonged benzene exposure may be delayed for many months or years after the actual exposure has ceased and identification or correlation with benzene exposure must be sought out in the occupational history.

(4) **Treatment of acute toxic effects.** Remove from exposure immediately. Make sure you are adequately protected and do not risk being overcome by fumes. Give oxygen or artificial resuscitation if indicated. Flush eyes, wash skin if contaminated and remove all contaminated clothing. Symptoms of intoxication may persist following severe exposures. Recovery from mild exposures is usually rapid and complete.

(5) **Surveillance and preventive considerations.**

(a) General. The principal effects of benzene exposure which form the basis for this regulation are pathological changes in the hematopoietic system, reflected by changes in the peripheral blood and manifesting clinically as pancytopenia, aplastic anemia, and leukemia. Consequently, the medical surveillance program is designed to observe, on a regular basis, blood indices for early signs of these effects, and although early signs of leukemia are not usually available, emerging diagnostic technology and innovative regimes make consistent surveillance for leukemia, as well as other hematopoietic effects, essential.

Initial examinations are to be provided within sixty days of the effective date of this standard, or at the time of initial assignment, and periodic examinations annually thereafter.

There are special provisions for medical tests in the event of hematologic abnormalities or for emergency situations.

The blood values which require referral to a hematologist or internist are noted in (b)(i) of this subsection. The standard specifies that blood abnormalities that persist must be referred "unless the physician has good reason to believe such referral is unnecessary" ((b)(i) of this subsection). Examples of conditions that could make a referral unnecessary despite abnormal blood limits are iron or folate deficiency, menorrhagia, or blood loss due to some unrelated medical abnormality.

Symptoms and signs of benzene toxicity can be nonspecific. Only a detailed history and appropriate investigative procedure will enable a physician to rule out or confirm conditions that place the employee at increased risk. To assist the examining physician with regard to which laboratory tests are necessary and when to refer an employee to the specialist, OSHA has established the following guidelines.

(b) Hematology guidelines. A minimum battery of tests is to be performed by strictly standardized methods.

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(i) Red cell, white cell, platelet counts, white blood cell differential, hematocrit and red cell indices must be performed by an accredited laboratory. The normal ranges for the red cell and white cell counts are influenced by altitude, race, and sex, and therefore should be determined by the accredited laboratory in the specific area where the tests are performed.

Either a decline from an absolute normal or an individual's baseline to a subnormal value or a rise to a supra-normal value, are indicative of potential toxicity, particularly if all blood parameters decline. The normal total white blood count is approximately 7,200/mm^3 plus or minus 3,000. For cigarette smokers the white count may be higher and the upper range may be 2,000 cells higher than normal for the laboratory. In addition, infection, allergies and some drugs may raise the white cell count. The normal platelet count is approximately 250,000 with a range of 140,000 to 400,000. Counts outside this range should be regarded as possible evidence of benzene toxicity.

Certain abnormalities found through routine screening are of greater significance in the benzene-exposed worker and require prompt consultation with a specialist, namely:

(A) Thrombocytopenia.

(B) A trend of decreasing white cell, red cell, or platelet indices in an individual over time is more worrisome than an isolated abnormal finding at one test time. The importance of trend highlights the need to compare an individual's test results to baseline and/or previous periodic tests.

(C) A constellation or pattern of abnormalities in the different blood indices is of more significance than a single abnormality. A low white count not associated with any abnormalities in other cell indices may be a normal statistical variation, whereas if the low white count is accompanied by decreases in the platelet and/or red cell indices, such a pattern is more likely to be associated with benzene toxicity and merits thorough investigation.

Anemia, leukopenia, macrocytosis or an abnormal differential white blood cell count should alert the physician to further investigate and/or refer the patient if repeat tests confirm the abnormalities. If routine screening detects an abnormality, follow-up tests which may be helpful in establishing the etiology of the abnormality are the peripheral blood smear and the reticulocyte count.

The extreme range of normal for reticulocytes is 0.4 to 2.5 percent of the red cells, the usual range being 0.5 to 1.2 percent of the red cells, but the typical value is in the range of 0.8 to 1.0 percent. A decline in reticulocytes to levels of less than 0.4 percent is to be regarded as possible evidence (unless another specific cause is found) of benzene toxicity requiring accelerated surveillance. An increase in reticulocyte levels to about 2.5 percent may also be consistent with (but is not as characteristic of) benzene toxicity.

(ii) An important diagnostic test is a careful examination of the peripheral blood smear. As with reticulocyte count the smear should be with fresh uncoagulated blood obtained from a needle tip following venipuncture or from a drop of earlobe blood (capillary blood). If necessary, the smear may, under certain limited conditions, be made from a blood sample

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anticoagulated with EDTA (but never with oxalate or heparin). When the smear is to be prepared from a specimen of venous blood which has been collected by a commercial Vacutainer type tube containing neutral EDTA, the smear should be made as soon as possible after the venesection. A delay of up to twelve hours is permissible between the drawing of the blood specimen into EDTA and the preparation of the smear if the blood is stored at refrigerator (not freezing) temperature.

(iii) The minimum mandatory observations to be made from the smear are:

(A) The differential white blood cell count;

(B) Description of abnormalities in the appearance of red cells; and

(C) Description of any abnormalities in the platelets.

(D) A careful search must be made throughout of every blood smear for immature white cells such as band forms (in more than normal proportion, i.e., over ten percent of the total differential count), any number of metamyelocytes, myelocytes, or myeloblasts. Any nucleate or multinucleated red blood cells should be reported. Large "giant" platelets or fragments of megakaryocytes must be recognized.

An increase in the proportion of band forms among the neutrophilic granulocytes is an abnormality deserving special mention, for it may represent a change which should be considered as an early warning of benzene toxicity in the absence of other causative factors (most commonly infection). Likewise, the appearance of metamyelocytes, in the absence of another probable cause, is to be considered a possible indication of benzene-induced toxicity.

An upward trend in the number of basophils, which normally do not exceed about 2.0 percent of the total white cells, is to be regarded as possible evidence of benzene toxicity. A rise in the eosinophil count is less specific but also may be suspicious of toxicity if it rises above 6.0 percent of the total white count.

The normal range of monocytes is from 2.0 to 8.0 percent of the total white count with an average of about 5.0 percent. About twenty percent of individuals reported to have mild but persisting abnormalities caused by exposure to benzene show a persistent monocytosis. The findings of a monocyte count which persists at more than ten to twelve percent of the normal white cell count (when the total count is normal) or persistence of an absolute monocyte count in excess of $800/mm^3$ should be regarded as a possible sign of benzene-induced toxicity.

A less frequent but more serious indication of benzene toxicity is the finding in the peripheral blood of the so-called "pseudo" (or acquired) Pelger-Huet anomaly. In this anomaly many, or sometimes the majority, of the neutrophilic granulocytes possess two round nuclear segments-less often one or three round segments-rather than three normally elongated segments. When this anomaly is not hereditary, it is often but not invariably predictive of subsequent leukemia. However, only about two percent of patients who ultimately develop acute myelogenous leukemia show the acquired Pelger-Huet anomaly. Other tests that can be administered to investigate blood abnormalities are discussed below; however, such procedures should be undertaken by the hematologist.

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An uncommon sign, which cannot be detected from the smear, but can be elicited by a "sucrose water test" of peripheral blood, is transient paroxysmal nocturnal hemoglobinuria (PNH), which may first occur insidiously during a period of established aplastic anemia, and may be followed within one to a few years by the appearance of rapidly fatal acute myelogenous leukemia. Clinical detection of PNH, which occurs in only one or two percent of those destined to have acute myelogenous leukemia, may be difficult; if the "sucrose water test" is positive, the somewhat more definitive Ham test, also known as the acid-serum hemolysis test, may provide confirmation.

(E) Individuals documented to have developed acute myelogenous leukemia years after initial exposure to benzene may have progressed through a preliminary phase of hematologic abnormality. In some instances pancytopenia (i.e., a lowering in the counts of all circulating blood cells of bone marrow origin, but not to the extent implied by the term "aplastic anemia") preceded leukemia for many years. Depression of a single blood cell type or platelets may represent a harbinger of aplasia or leukemia. The finding of two or more cytopenias, or pancytopenia in a benzene-exposed individual, must be regarded as highly suspicious of more advanced although still reversible, toxicity. "Pancytopenia" coupled with the appearance of immature cells (myelocytes, myeloblasts, erythroblasts, etc.), with abnormal cells (pseudo Pelger-Huet anomaly, atypical nuclear heterochromatin, etc.), or unexplained elevations of white blood cells must be regarded as evidence of benzene overexposure unless proved otherwise.

Many severely aplastic patients manifested the ominous finding of five to ten percent myeloblasts in the marrow, occasional myeloblasts and myelocytes in the blood and twenty to thirty monocytes. It is evident that isolated cytopenias, pancytopenias, and even aplastic anemias induced by benzene may be reversible and complete recovery has been reported on cessation of exposure. However, since any of these abnormalities is serious, the employee must immediately be removed from any possible exposure to benzene vapor. Certain tests may substantiate the employee's prospects for progression or regression. One such test would be an examination of the bone marrow, but the decision to perform a bone marrow aspiration or needle biopsy is made by the hematologist.

The findings of basophilic stippling in circulating red blood cells (usually found in one to five percent of red cells following marrow injury), and detection in the bone marrow of what are termed "ringed sideroblasts" must be taken seriously, as they have been noted in recent years to be premonitory signs of subsequent leukemia.

Recently peroxidase-staining of circulating or marrow neutrophil granulocytes, employing benzidine dihydrochloride, have revealed the disappearance of, or diminution in, peroxidase in a sizable proportion of the granulocytes, and this has been reported as an early sign of leukemia. However, relatively few patients have been studied to date. Granulocyte granules are normally strongly peroxidase positive. A steady decline in leukocyte alkaline phosphatase has also been reported as suggestive of early acute leukemia. Exposure to benzene may cause an early rise in serum iron, often but not always associated with a fall in the reticulocyte count. Thus, serial measurements of serum iron levels may provide a means of determining whether or not there is a trend representing sustained suppression of erythropoiesis.

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Measurement of serum iron, determination of peroxidase and of alkaline phosphatase activity in peripheral granulocytes can be performed in most pathology laboratories. Peroxidase and alkaline phosphatase staining are usually undertaken when the index of suspicion for leukemia is high.

[Statutory Authority: Chapter 49.17 RCW. 88-21-002 (Order 88-23), 296-62-07529, filed 10/6/88, effective 11/7/88.]

WAC 296-62-07531 Appendix D sampling and analytical methods for benzene monitoring and measurement procedures. Measurements taken for the purpose of determining employee exposure to benzene are best taken so that the representative average eight-hour exposure may be determined from a single eight-hour sample or two four-hour samples. Short-time interval samples (or grab samples) may also be used to determine average exposure level if a minimum of five measurements are taken in a random manner over the eight-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random samples taken on one work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analysis must be performed with procedures meeting the requirements of the standard.

There are a number of methods available for monitoring employee exposures to benzene. The sampling and analysis may be performed by collection of the benzene vapor on charcoal adsorption tubes, with subsequent chemical analysis by gas chromatography. Sampling and analysis may also be performed by portable direct reading instruments, real-time continuous monitoring systems, passive dosimeters or other suitable methods. The employer has the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the standard under his unique field conditions. The standard requires that the method of monitoring must have an accuracy, to a ninety-five percent confidence level, of not less than plus or minus twenty-five percent for concentrations of benzene greater than or equal to 0.5 ppm.

The WISHA laboratory uses NIOSH Method 1500 for evaluation of benzene air concentrations.

(1) **WISHA method HYDCB for air samples.**

Analyte: Benzene.

Matrix: Air.

Procedure: Adsorption on charcoal, desorption with carbon disulfide, analysis by GC.

Detection limit: 0.04 ppm.

Recommended air volume and sampling rate: 10L at 0.05 to 0.2 L/min.

(a) Principle of the method.

(i) A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

(ii) The charcoal in the tube is transferred to a small, stoppered vial, and the analyte is desorbed with carbon disulfide.

(iii) An aliquot of the desorbed sample is injected into a gas chromatograph.

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(iv) The area of the resulting peak is determined and compared with areas obtained from standards.

(b) Advantages and disadvantages of the method.

(i) The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples are analyzed by means of a quick, instrumental method.

(ii) The amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds twenty-five percent of that found on the front section, the possibility of sample loss exists.

(c) Apparatus.

(i) A calibrated personal sampling pump whose flow can be determined within ±5 percent at the recommended flow rate.

(ii) Charcoal tubes: Glass with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is obtained commercially. The adsorbing section contains 100 mg of charcoal, the back-up section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the back-up section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of one liter per minute.

(iii) Gas chromatograph equipped with a flame ionization detector.

(iv) Column (10-ft 1/8-in stainless steel) packed with 80/100 Supelcoport coated with twenty percent SP 2100, 0.1 percent CW 1500.

(v) An electronic integrator or some other suitable method for measuring peak area.

(vi) Two-milliliter sample vials with Teflon-lined caps.

(vii) Microliter syringes: 10-microliter 10-uL syringe, and other convenient sizes for making standards, 1-uL syringe for sample injections.

(viii) Pipets: 1.0 mL delivery pipets.

(ix) Volumetric flasks: Convenient sizes for making standard solutions.

(d) Reagents.

(i) Chromatographic quality carbon disulfide (CS2). Most commercially available carbon disulfide contains a trace of benzene which must be removed. It can be removed with the following procedure:

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Heat under reflux for two to three hours, 500 mL of carbon disulfide, 10 mL concentrated sulfuric acid, and five drops of concentrated nitric acid. The benzene is converted to nitrobenzene. The carbon disulfide layer is removed, dried with anhydrous sodium sulfate, and distilled. The recovered carbon disulfide should be benzene free. (It has recently been determined that benzene can also be removed by passing the carbon disulfide through 13x molecular sieve.)

(ii) Benzene, reagent grade.

(iii) p-Cymene, reagent grade, (internal standard).

(iv) Desorbing reagent. The desorbing reagent is prepared by adding 0.05 mL of p-Cymene per milliliter of carbon disulfide. (The internal standard offers a convenient means correcting analytical response for slight inconsistencies in the size of sample injections. If the external standard technique is preferred, the internal standard can be eliminated.)

(v) Purified GC grade helium, hydrogen, and air.

(e) Procedure.

(i) Cleaning of equipment. All glassware used for the laboratory analysis should be properly cleaned and free of organics which could interfere in the analysis.

(ii) Calibration of personal pumps. Each pump must be calibrated with a representative charcoal tube in the line.

(iii) Collection and shipping of samples.

(A) Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

(B) The smaller section of the charcoal is used as the backup and should be placed nearest the sampling pump.

(C) The charcoal tube should be placed in a vertical position during sampling to minimize channeling through the charcoal.

(D) Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

(E) A sample size of ten liters is recommended. Sample at a flow rate of approximately 0.05 to 0.2 liters per minute. The flow rate should be known with an accuracy of at least ±5 percent.

(F) The charcoal tubes should be capped with the supplied plastic caps immediately after sampling.

(G) Submit at least one blank tube (a charcoal tube subjected to the same handling procedures, without having any air drawn through it) with each set of samples. Take necessary shipping and packing precautions to minimize breakage of samples.

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(iv) Analysis of samples.

(A) Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml vial. The separating section of foam is removed and discarded; the second section is transferred to another capped vial. These two sections are analyzed separately.

(B) Desorption of samples. Prior to analysis, 1.0 mL of desorbing solution is pipetted into each sample container. The desorbing solution consists of 0.05 uL internal standard per mL of carbon disulfide. The sample vials are capped as soon as the solvent is added. Desorption should be done for thirty minutes with occasional shaking.

(C) GC conditions. Typical operating conditions for the gas chromatograph are:

(I) 30 mL/min (60 psig) helium carrier gas flow.

(II) 30 mL/min (40 psig) hydrogen gas flow to detector.

(III) 240 mL/min (40 psig) air flow to detector.

(IV) 150°C injector temperature.

(V) 250°C detector temperature.

(VI) 100°C column temperature.

(D) Injection size. 1 µL.

(E) Measurement of area. The peak areas are measured by an electronic integrator or some other suitable form of area measurement.

(F) An internal standard procedure is used. The integrator is calibrated to report results in ppm for a ten liter air sample after correction for desorption efficiency.

(v) Determination of desorption efficiency.

(A) Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and from one lot of chemical to another. Thus, it is necessary to determine, at least once, the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

(B) Procedure for determining desorption efficiency. The reference portion of the charcoal tube is removed. To the remaining portion, amounts representing 0.5X, 1X, and 2X and (X represents target concentration) based on a 10 L air sample are injected into several tubes at each level. Dilutions of benzene with carbon disulfide are made to allow injection of measurable quantities. These

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tubes are then allowed to equilibrate at least overnight. Following equilibration they are analyzed following the same procedure as the samples. Desorption efficiency is determined by dividing the amount of benzene found by amount spiked on the tube.

(f) Calibration and standards. A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions that will be used on the samples. A calibration curve is prepared by plotting concentration (mg/mL) versus peak area.

(g) Calculations. Benzene air concentration can be calculated from the following equation:

$mg/m^3 = (A)(B)/(C)(D)$

Where: A = µg/mL benzene, obtained from the calibration curve

B = desorption volume (1 mL)

C = Liters of air sampled

D = desorption efficiency

The concentration in mg/m^3 can be converted to ppm (at 25° C and 760 mm) with the following equation:

$ppm = (mg/m^3)(24.46)/(78.11)$

Where: 24.46 = molar volume of an ideal gas 25° C and 760 mm

78.11 = molecular weight of benzene

(h) Backup data.

(i) Detection limit-air samples.

The detection limit for the analytical procedure is 1.28 mg with a coefficient of 0.04 ppm for a 10 L air sample. This amount provided a chromatographic peak that could be identifiable in the presence of possible interferences. The detection limit data were obtained by making 1 µL injections of a 1.283 µg/mL standard.

TABLE 1		
Injection	**Area Count**	
1	655.4	
2	617.5	
3	662.0	$\bar{X}$ = 640.2
4	641.1	SD = 14.9
5	636.4	CV = 0.023
6	629.2	

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(ii) Pooled coefficient of variation-Air Samples. The pooled coefficient of variation for the analytical procedure was determined by 1 uL replicate injections of analytical standards. The standards were 16.04, 32.08, and 64.16 μg/mL, which are equivalent to 0.5, 1.0, and 2.0 ppm for a 10 L air sample respectively.

TABLE 2			
	Area Count		
Injection	0.5 ppm	1.0 ppm	2.0 ppm
1	3996.5	8130.2	16481
2	4059.4	8235.6	16493
3	4052.0	8307.9	16535
4	4027.2	8263.2	16609
5	4046.3	8291.1	16552
6	4137.9	8288.8	16618
$\bar{X}$ =	4053.3	8254.0	16548.3
SD =	47.2	62.5	57.1
CV =	0.0116	0.0076	0.0034
CV =			

(iii) Storage data-air samples.

Samples were generated at 1.03 ppm benzene at eighty percent relative humidity, 22° C, and 643 mm. All samples were taken for fifty minutes at 0.2 L/min. Six samples were analyzed immediately and the rest of the samples were divided into two groups by fifteen samples each. One group was stored at refrigerated temperature of –25° C, and the other group was stored at ambient temperature (approximately 23° C). These samples were analyzed over a period of fifteen days. The results are tabulated below.

TABLE 3						
Day analyzed	Refrigerated			Ambient		
0	97.4	98.7	98.9	97.4	98.7	98.9
0	97.1	100.5	100.9*	97.1	100.6	100.9
2	95.8	96.4	95.4	95.4	96.6	96.9
5	93.9	93.7	92.4	92.4	94.3	94.1
9	93.6	95.5	94.6	95.2	95.6	96.6
13	94.3	95.3	93.7	91.0	95.0	94.6
15	96.6	95.8	94.2	92.9	96.3	95.9

(iv) Desorption data.

Samples were prepared by injecting liquid benzene onto the A section of charcoal tubes. Samples were prepared that would be equivalent to 0.5, 1.0, and 2.0 ppm for a 10 L air sample.

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TABLE 4			
Sample	**0.5 ppm**	**1.0 ppm**	**2.0 ppm**
1	99.4	98.8	99.5
2	99.5	98.7	99.7
3	99.2	98.6	99.2
4	99.4	99.1	100.0
5	99.2	99.0	99.7
6	99.8	99.1	99.9
$\bar{X}$ =	99.4	98.9	99.8
SD =	.22	0.21	0.18
CV =	0.0022	0.0021	0.0018
$\bar{X}$ = 99.4			

(v) Carbon disulfide.

Carbon disulfide from a number of sources was analyzed for benzene contamination. The results are given in the following table. The benzene contaminant can be removed with the procedures given in (d)(i) of this subsection.

TABLE 5		
SAMPLE	**µG Benzene/mL**	**ppm equivalent (for 10 l air sample**
Aldrich Lot 83017	4.20	0.13
Baker Lot 720364	1.0†	0.03
Baker Lot 822351	1.0†	0.03
Malinkrodt Lot WEMP	1.74	0.05
Malinkrodt Lot WHGA	5.65	0.18
Treated CS^2	2.90	0.09

(2) **WISHA laboratory method for bulk samples.**

Analyte: Benzene.

Matrix: Bulk samples.

Procedure: Bulk samples are analyzed directly by high performance liquid chromatography (HPLC) or by capillary gas chromatography. See laboratory manual for GC procedure.

Detection limits: 0.01% by volume.

(a) Principle of the method.

(i) An aliquot of the bulk sample to be analyzed is injected into a liquid chromatograph or gas chromatograph.

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(ii) The peak area for benzene is determined and compared to areas obtained from standards.

(b) Advantages and disadvantages of the method.

(i) The analytical procedure is quick, sensitive, and reproducible.

(ii) Reanalysis of samples is possible.

(iii) Interferences can be circumvented by proper selection of HPLC parameters or GC parameters.

(iv) Samples must be free of any particulates that may clog the capillary tubing in the liquid chromatograph. This may require distilling the sample or clarifying with a clarification kit.

(c) Apparatus.

(i) Liquid chromatograph equipped with a UV detector or capillary gas chromatograph with FID detector.

(ii) HPLC column that will separate benzene from other components in the bulk sample being analyzed. The column used for validation studies was a Waters uBondapack C18, 30 cm x 3.9 mm.

(iii) A clarification kit to remove any particulates in the bulk if necessary.

(iv) A micro-distillation apparatus to distill any samples if necessary.

(v) An electronic integrator or some other suitable method of measuring peak areas.

(vi) Microliter syringes-10 µL syringe and other convenient sizes for making standards. 10 µL syringe for sample injections.

(vii) Volumetric flasks, 5 mL and other convenient sizes for preparing standards and making dilutions.

(d) Reagents.

(i) Benzene, reagent grade.

(ii) HPLC grade water, methyl alcohol, and isopropyl alcohol.

(e) Collection and shipment of samples.

(i) Samples should be transported in glass containers with Teflon-lined caps.

(ii) Samples should not be put in the same container used for air samples.

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(f) Analysis of samples.

(i) Sample preparation.

If necessary, the samples are distilled or clarified. Samples are analyzed undiluted. If the benzene concentration is out of the working range, suitable dilutions are made with isopropyl alcohol.

(ii) HPLC conditions.

The typical operating conditions for the high performance liquid chromatograph are:

(A) Mobile phase-Methyl alcohol/water, 50/50.

(B) Analytical wavelength-254 nm.

(C) Injection size-10 µL.

(iii) Measurement of peak area and calibration.

Peak areas are measured by an integrator or other suitable means. The integrator is calibrated to report results % in benzene by volume.

(g) Calculations.

Since the integrator is programmed to report results in % benzene by volume in an undiluted sample, the following equation is used:

% Benzene by Volume = A x B

Where: A = % by volume on report

B = Dilution Factor

(B = 1 for undiluted sample)

(h) Backup data.

(i) Detection limit-bulk samples.

The detection limit for the analytical procedure for bulk samples is 0.88 µg, with a coefficient or variation of 0.019 at this level. This amount provided a chromatographic peak that could be identifiable in the presence of possible interferences. The detection limit data were obtained by making 10 µL injections of a 0.10% by volume standard.

TABLE 6		
1	45386	
2	44214	
3	43822	$\bar{X}$ = 44040.1
4	44062	SD = 852.5
6	42724	CV = 0.019

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(ii) Pooled coefficient of variation-bulk samples.

The pooled coefficient of variation for analytical procedure was determined by 50 µL replicate injections of analytical standards. The standards were 0.01, 0.02, 0.04, 0.10, 1.0, and 2.0% benzene by volume.

TABLE 7

Injection No.	0.01	0.02	0.04	0.10	1.0	2.0
1	45386	84737	166097	448497	4395380	9339150
2	44241	84300	170832	441299	4590800	9484900
3	43833	83835	164160	443719	4593200	9557580
4	44062	84381	164445	444842	4642350	9677060
5	44006	83012	168398	442564	4646430	9766240
6	42724	81957	173002	443975	4646260	------
_						
X	44040.1	83703.6	167872	444149	4585767	9564986
SD =	852.5	1042.2	3589.8	2459.1	96839.3	166233
CV =	0.0194	0.0125	0.0213	0.0055	0.0211	0.0174
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CV =	0.017					

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